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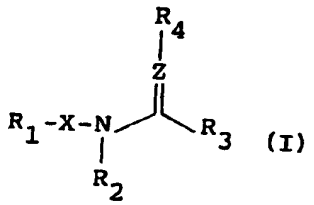
(54) Title: AMINE DERIVATIVES



(I)

(57) Abstract

The present invention relates to a compound having formula (I) which has an excellent insecticidal activity, wherein R_1 represents an optionally substituted 5-6 membered aromatic hetero ring containing nitrogen atom, except a non-substituted 2-pyridyl; X represents an optionally substituted C_{1-3} alkylene or alkylidene; R_2 represents a hydrogen, a carbamoyl, a mono or di C_{1-5} alkyl carbamoyl, a thiocarbamoyl, a mono or di C_{1-5} alkylthiocarbamoyl, a sulfamoyl, a mono or di C_{1-5} alkylsulfamoyl, an optionally substituted C_{1-5} alkyl, an optionally substituted C_{2-5} alkenyl, an optionally substituted C_{2-5} alkynyl, an optionally substituted C_{3-8} cycloalkyl, an optionally substituted C_{3-8} cycloalkenyl, an optionally substituted aryl or -Y-R_5; Y represents O, $S(O)_n$, CO, CS or CO_2; n represents 0, 1 or 2; R_5 represents a hydrogen, an optionally substituted C_{1-5} alkyl, an optionally substituted C_{2-5} alkenyl, an optionally substituted C_{2-5} alkynyl, an optionally substituted C_{3-8} cycloalkyl, an optionally substituted C_{3-8} cycloalkenyl or an optionally substituted aryl; R_3 represents a hydrogen, an optionally substituted C_{1-5} alkyl, an optionally substituted C_{2-5} alkenyl, an optionally substituted C_{2-5} alkynyl, an optionally substituted C_{3-8} cycloalkyl or an optionally substituted C_{3-8} cycloalkenyl; R_4 represents a cyano or a nitro; and Z represents CH or N; or its salt.

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DESCRIPTION

Amine Derivatives

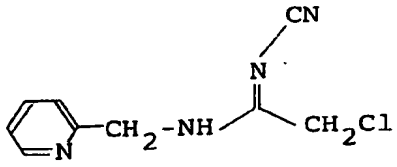
Technical Field:

The present invention relates to new amine derivatives, the processes for the production thereof and insecticides containing the said derivatives as effective compounds.

Background art:

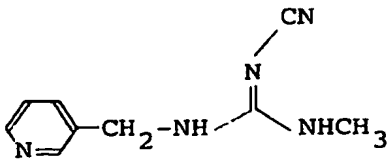
A large number of chemicals, for example, organophosphorus insecticides such as parathion and malathion and carbamate insecticides such as carbaryl and methomyl, have been developed and put to practical use by research and development on insecticides over many years. These insecticedes have played a very great role for the improvement of agricultural production. However, in recent years some of these insecticides are regulated on their use because of problems such as environmental pollution due to residue or accumulation, or cause infestitation of resistant insect pests as a result of long-term use. Therefore, it is demanded to develop new chemicals which have excellent insecticidal characteristics over various types of insect pests including these resistant insect pests and which can be used safely.

The following compound is known as the analogous compound of this invention, which has no insecticidal activity.



(Boll. Chim. Farm., 1979 118(11)661-666)

Further, the following compound is described in USP 4918088, which has insecticidal activities.



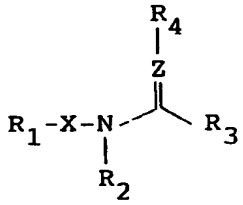
The compound however shows no insecticidal activity against lepidopterous insects and green rice leafhopper which are more serious pests on crops, though it shows the activity against cotton aphid.

The purpose of this invention is to provide agricultural chemicals which can be advantageously synthesized industrially, have certain effects and are applicable safely.

The compound of this invention has high insecticidal activity against both lepidopterous and hemipterous insects.

Disclosure of Invention:

The present invention relates to a compound having the formula



(I)

wherein R_1 represents an optionally substituted 5 - 6 membered aromatic hetero ring containing nitrogen atom, except a non-substituted 2-pyridyl;

X represents an optionally substituted C_{1-3} alkylene or alkylidene;

R_2 represents a hydrogen, a carbamoyl, a mono or di C_{1-5} alkyl carbamoyl, a thiocarbamoyl, a mono or di C_{1-5} alkylthiocarbamoyl, a sulfamoyl, a mono or di C_{1-5}

alkylsulfamoyl, an optionally substituted C_{1-5} alkyl, an optionally substituted C_{2-5} alkenyl, an optionally substituted C_{2-5} alkynyl, an optionally substituted C_{3-8} cycloalkyl, an optionally substituted C_{3-8} cycloalkenyl, an optionally substituted aryl or $-Y-R_5$;

Y represents O, $S(O)_n$, CO, CS or CO_2;

n represents 0,1 or 2;

R_5 represents a hydrogen, an optionally substituted C_{1-5} alkyl, an optionally substituted C_{2-5} alkenyl, an optionally substituted C_{2-5} alkynyl, an optionally substituted C_{3-8} cycloalkyl, an optionally substituted C_{3-8} cycloalkenyl or an optionally substituted aryl;

R_3 represents a hydrogen, an optionally substituted C_{1-5} alkyl, an optionally substituted C_{2-5} alkenyl, an optionally substituted C_{2-5} alkynyl, an optionally substituted C_{3-8} cycloalkyl or an optionally substituted C_{3-8} cycloalkenyl;

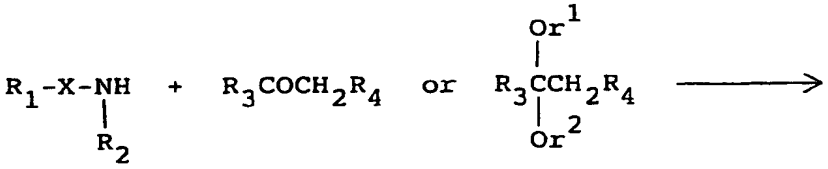
R_4 represents a cyano or a nitro; and Z represents CH or N;

or its salt.

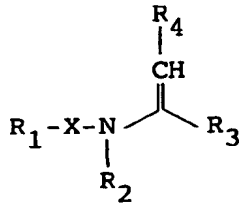
Best Mode for Carrying Out the Invention:

The compounds of this invention can be prepared in accordance with the following reaction schemes:

(1) Preparation Method 1:



(II) (III) (III)'

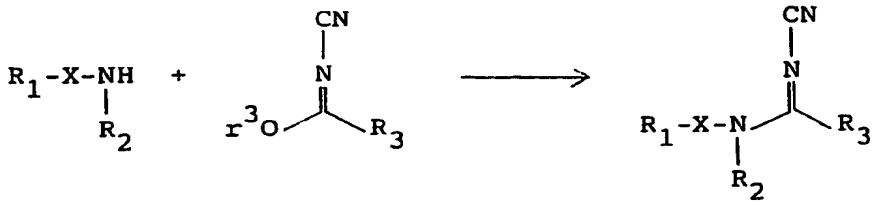


(I')

where r^1 and r^2 represent a C_{1-5} alkyl; and R_1, R_2, R_3, R_4 and X are as defined above.

The reaction is carried out in an inactive organic solvent, preferably in an aromatic hydrocarbon solvent such as xylene, toluene or benzene, in the presence of acidic catalyst such as p-toluenesulfonic acid, if necessary, under reflux.

(2) Preparation method 2:

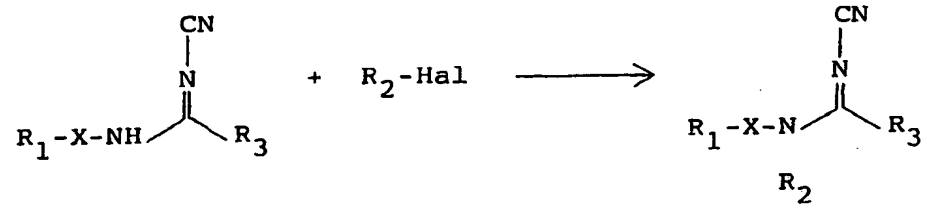


(II) (IV) (I")

where r^3 represents a C_{1-5} alkyl:

and R_1, R_2, R_3 and X are as defined above. This reaction is carried out in an inactive organic solvent, preferably in an alcohol such as methanol, ethanol, between room temperature and the boiling point of the used solvent.

(3) Preparation Method 3:

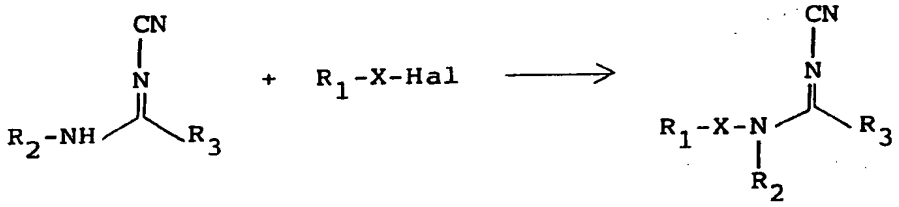


(I''') (V) (I")

where Hal represents a halogen; and R_1, R_2, R_3 and X are as defined above.

This reaction is carried out in an inactive organic solvent, preferably DMF, THF, benzene acetonitrile, acetone, methylethylketone, in the presence of acid accepter such as potassium carbonate, NaH, triethylamine, between room temparature and the boiling point of the used solvent.

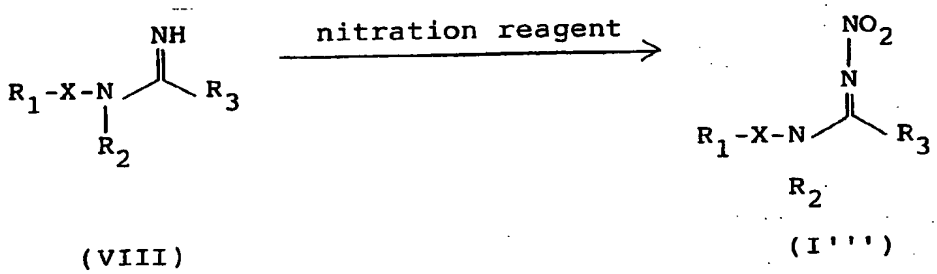
(4) Preparation Method 4:



(VI) (VII) (I")

where R_1, R_2, R_3, X and Hal are as defined above. This reaction is carried out in the same manner as that of Preparation Method 3.

(5) Preparation Method 5:

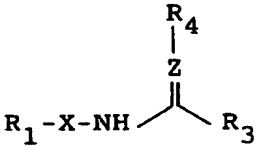


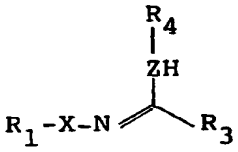
(VIII) (I''')

where R_1, R_2, R_3 and X are as defined above. This reaction is carried out in an inactive organic solvent, preferably acetonitrile, carbon tetrachloride, dichloroethane, in the presence of nitration reagent such as nitronium tetrafluoroborate, between -20°C and the boiling point of the used solvent.

After the reaction is completed, an usual after-treatment gives the intended compound. The structure of the compounds of this invention was determined by such means as IR, NMR, MASS, etc.

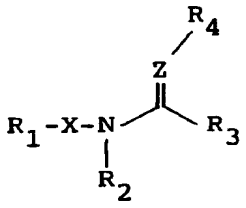
When R_2 is hydrogen in a compound of this invention, tautomers represented by

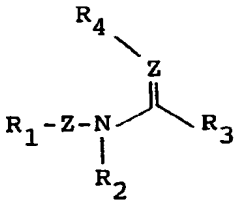




can exist.

The syn - aniti isomers, when Z represents N, and the cis-trans isomers, when Z represents CH, as represented by,



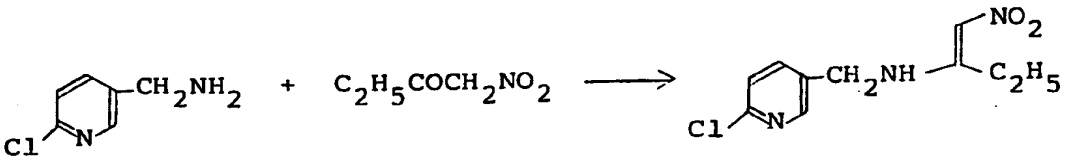


can also exist.

The ratio varies depending on e.g. conditions of instrumental analysis.

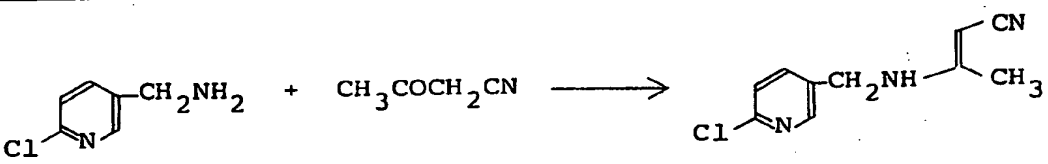
The following examples illuslrate the present invention.

Example 1 : 2-(2-chloro-5-pyridylmethylamino)-1-nitro-1-butene:



In 50ml of toluene, 4.2g of 2-chloro-5-pyridylmethylamine, 3.5g of 1-nitro-2-butanone and 0.1g of p-toluene sulfonic acid were mixed and the mixture was refluxed for 2 hours. The solvent was then distilled off and the residue was purified by column chromatography on silica gel to afford 4.1g of compound No. 368. m.p. 95-98°C

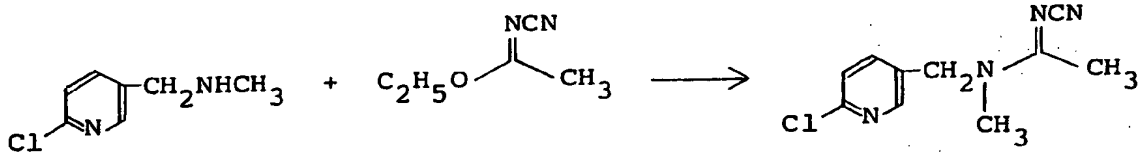
Example 2 : 2-(2-chloro-5-pyridylmethylamino)-1-cyano-1-propene:



1.4g of 2-chloro-5-pyridylmethylamine and 0.8g of 1-cyano-2-propanone were mixed and the mixture was stirred at room temperature over night. The solvent was then distilled off and the residue was purified by column chromatography on silica gel to afford 1.7g of compound No. 528. m.p. 95-98°C

Example 3 :

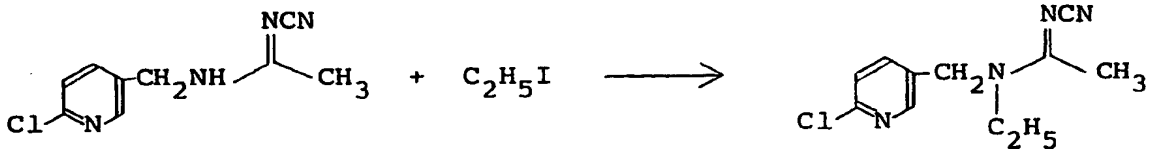
N-cyano-N'-(2-chloro-5-pyridylmethyl)-N'-methylacetamidine:



In 20ml of ethanol, 1.6g of N-methyl-2-cloro-5-pyridylmethylamine and 1.2g of ethyl-N-cyanoacetamidine were mixed and the mixture was stirred at room temperature over night. The solvent was then distilled off and the residue was purified by column chromatography on silica gel to afford 1.8g of compound No. 22. m.p. 101-103°C

Example 4 :

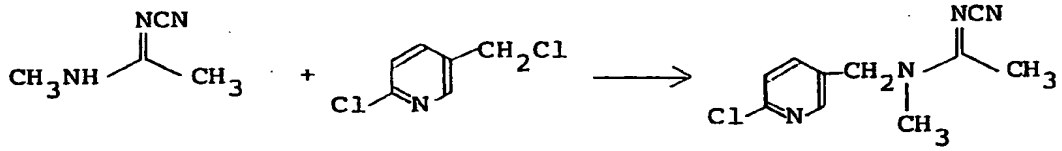
N-cyano-N'-(2-chloro-5-pyridylmethyl)-N'-ethylacetamidine:



0.7g of sodium hydride (purity 60%) was added to the solution of 3.0g of N-cyano-N'-(2-chloro-5-pyridylmethyl)acetamidine in 20ml of N.N-dimthylformamide at ice bath temperature. After stirring it at the same temperature for 1 hour, 2.7g of ethyl iodide was added to the mixture, followed by stirring for 5 hours at room temperature. The reaction mixture was then poured into ice-water, extracted with ethyl acetate, dried over anhydrous magnesium sulfate and concentrated under reduced pressre. The residue obtained was purified by column chromatography on silica gel to afford 1.6g of compound No. 51. m.p. 100-101°C

Example 5 :

N-cyano-N-(2-chloro-5-pyridylmethyl)-N'-methylacetamidine:

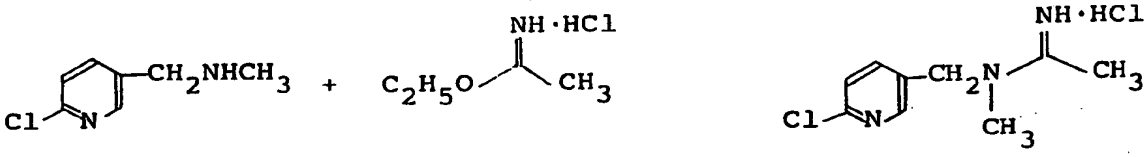


0.6g of sodium hydride (purity 60%) was added to the solution of 1.3g of N-cyano-N'-methylacetamidine in 20ml of N,N-dimethylformamide at ice bath temperature. After stirring it at the same temperature for 1 hour, 2.2g of 2-chloro-5-pyridylmethylchlride was added to the mixture, followed by stirring for 5 hours at room temperature. The reaction mixture was then poured into ice-water, extrated with ethyl acetate, dried over

anhydrous magnesium sulfate and concentrated under reduced pressre. The residue obtained was purified by column chromatography on silica gel to afford 1.5g of compound No.22 m.p. 101-103°C

Reference Example :

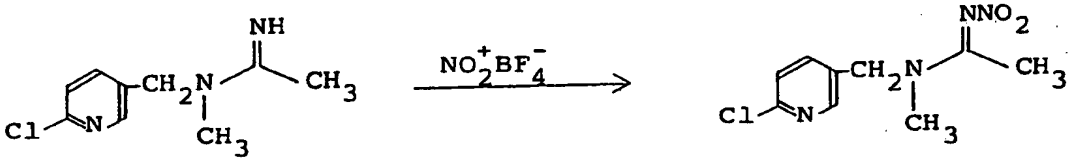
N-(2-chloro-5-pyridylmethyl)-N-methylacetamidine hydrochloride :



To 40ml of ethanol was added 5.1g of N-(2-chloro-5-pyridylmethyl)-N-Methylamine and then 4g of ethyl acetimidate hydrochloride at 0°C. After stirring for an hour, the reaction mixture was allowed to warm to room temperature and stirred over night. The solvent was then distilled off. The obtained white residue was washed with diethyl ether to afford 7.3g of the title compound m.p. 192-197°C

Example 6 :

N-(2-chloro-5-pyridylmethyl)-N-methyl-N'-nitroacetamidine:



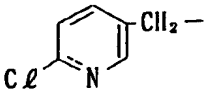
To a suspension of 1g of N-(2-chloro-5-pyridylmethyl)-N-methylamidine hydrochloride in 10ml of dry acetonitrile was added dropwise 0.7g of DBU under nitrogen at room temperature. After stirring for 30 minutes, the solution was added dropwise to a suspension of 0.6g of nitronium tetrafluoroborate in 5ml of dry acetonitrile under nitrogen on cooling with ice-water and let stir for 4 hours. After which time, the mixture was poured into ice-water, then extracted several time with chloroform. The combined chloroform layer was dried over magnesium sulfate, filtered and

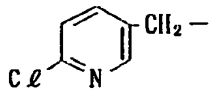
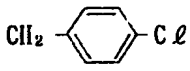
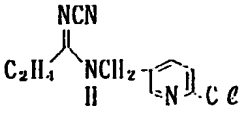
distilled off. The crude oil was purified by column chromatgraphy on silica gel to afford 0,3g of compound No. 236.

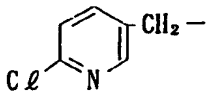
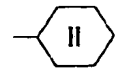
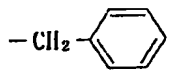
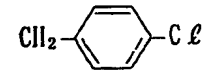
N_D^{25} 1.5808

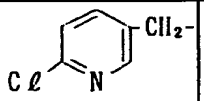
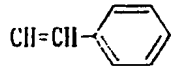
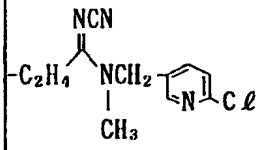
Typical examples of this invention including those described above are listed in Table 1.

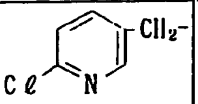
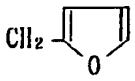
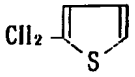
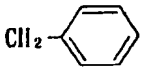
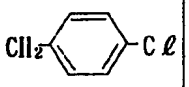
Table 1

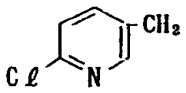
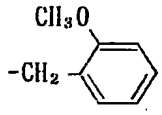
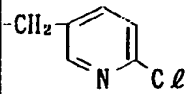
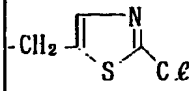
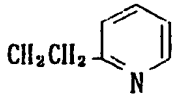
Compound No.	Structure Formula					Physical Properties
	R_1X	R_2	R_3	Z	R_4	( ) m.p.℃
1		H	H	N	CN	(123-126)
2	〃	〃	CH_3	〃	〃	(141-143)
3	〃	〃	$CH_2C\ell$	〃	〃	(124-126)
4	〃	〃	CH_2F	〃	〃	(151-152)
5	〃	〃	CF_3	〃	〃	(112-114)
6	〃	〃	C_2H_5	〃	〃	(120-122)
7	〃	〃	$C_3H_7(n)$	〃	〃	(100-101)
8	〃	〃		〃	〃	(193.5-195)
9	〃	〃	$C_4H_9(t)$	〃	〃	
10	〃	〃	CH_2OCH_3	〃	〃	(128-128.5)
11	〃	〃	CH_2SCH_3	〃	〃	(116-118)

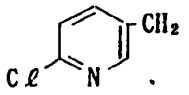
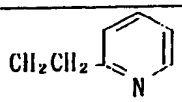
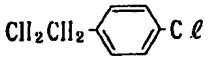
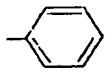
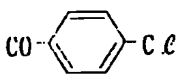
No.	R_1X	R_2	R_3	Z	R_4	[ ] m.p.℃
12		H	$CH_2COOC_2H_5$	N	CN	$n_D^{25.5}$ 1.5608
13	〃	〃	$CH_2CH_2COOC_2H_5$	〃	〃	
14	〃	〃	CH_2NHCH_3	〃	〃	
15	〃	〃	$CH_2N(CH_3)_2$	〃	〃	
16	〃	〃	$CH_2CH_2CH_2C\ell$	〃	〃	[114-115]
17	〃	〃		〃	〃	[190-191]
18	〃	〃	CH_2CN	〃	〃	[106-108]
19	〃	〃	CH_2CH_2CN	〃	〃	
20	〃	〃		〃	〃	[187-189]
21	〃	CH_3	H	〃	〃	n_D^{25} 1.5918
22	〃	〃	CH_3	〃	〃	[101-103]
23	〃	〃	〃	〃	〃	[161-162] HCℓ salt
24	〃	〃	$CH_2C\ell$	〃	〃	$n_D^{26.5}$ 1.5921
25	〃	〃	CH_2F	〃	〃	[79-80]
26	〃	〃	CF_3	〃	〃	＊1

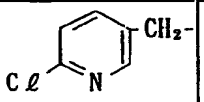
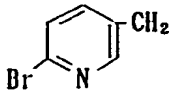
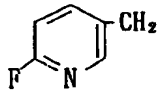
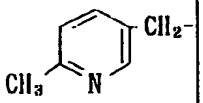
No.	R_1X	R_2	R_3	Z	R_4	[ ] m.p. ℃
27		CH_3	C_2H_5	N	CN	n_D^{27} 1.5742
28	〃	〃	C_3H_7(n)	〃	〃	[97-100]
29	〃	〃		〃	〃	$n_D^{24.5}$ 1.5829
30	〃	〃	C_4H_9(t)	〃	〃	
31	〃	〃	CH_2OCH_3	〃	〃	n_D^{24} 1.5803
32	〃	〃	CH_2SCH_3	〃	〃	$n_D^{24.5}$ 1.6070
33	〃	〃	$CH_2COOC_2H_5$	〃	〃	$n_D^{25.5}$ 1.5604
34	〃	〃	$CH_2CH_2COOC_2H_5$	〃	〃	$n_D^{24.5}$ 1.5605
35	〃	〃	CH_2NHCH_3	〃	〃	n_D^{25} 1.5861
36	〃	〃	$CH_2N(CH_3)_2$	〃	〃	n_D^{25} 1.5577
37	〃	〃	$CH_2CH_2C\ell$	〃	〃	
38	〃	〃	$CH_2CH_2CH_2C\ell$	〃	〃	$n_D^{25.5}$ 1.5830
39	〃	〃		〃	〃	
40	〃	〃		〃	〃	
41	〃	〃		〃	〃	$n_D^{25.5}$ 1.6040

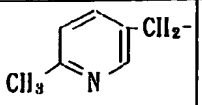
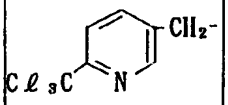
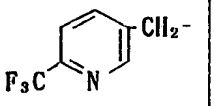
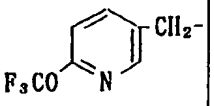
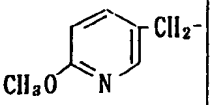
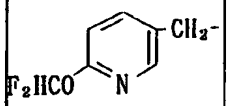
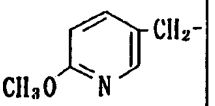
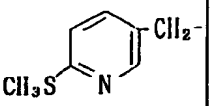
No.	R_1X	R_2	R_3	Z	R_4	[ ] m.p.℃
42		CH_3	$CH=CH_2$	N	CN	
43	〃	〃	CH_2CN	〃	〃	n_D^{25} 1.5913
44	〃	〃	CH_2CH_2CN	〃	〃	[112-114]
45	〃	〃		〃	〃	
46	〃	〃		〃	〃	[224-226]
47	〃	CHF_2	H	〃	〃	
48	〃	〃	CH_3	〃	〃	$n_D^{24.5}$ 1.5423
49	〃	〃	C_2H_5	〃	〃	
50	〃	C_2H_5	H	〃	〃	[101-103]
51	〃	〃	CH_3	〃	〃	[100-101]
52	〃	〃	C_2H_5	〃	〃	
53	〃	C_3H_7(i)	H	〃	〃	[205-207]
54	〃	〃	CH_3	〃	〃	
55	〃	〃	C_2H_5	〃	〃	
56	〃		H	〃	〃	

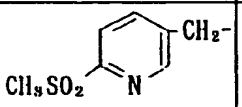
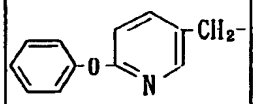
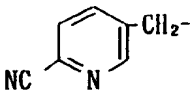
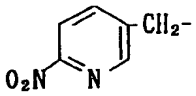
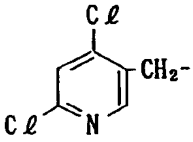
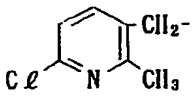
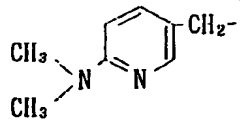
No.	R_1X	R_2	R_3	Z	R_4	[ ] m.p.℃
57			CH_3	N	CN	n_D^{25} 1.5825
58	〃	〃	C_2H_5	〃	〃	
59	〃	CH_2OCH_3	H	〃	〃	
60	〃	〃	CH_3	〃	〃	$n_D^{25.5}$ 1.5711
61	〃	CH_2SCH_3	H	〃	〃	
62	〃	〃	CH_3	〃	〃	n_D^{25} 1.5828
63	〃	$CH_2COOC_2H_5$	H	〃	〃	
64	〃	〃	CH_3	〃	〃	n_D^{25} 1.5475
65	〃		H	〃	〃	
66	〃	〃	CH_3	〃	〃	$n_D^{25.5}$ 1.5928
67	〃		H	〃	〃	
68	〃	〃	CH_3	〃	〃	$n_D^{25.5}$ 1.6155
69	〃		H	〃	〃	
70	〃	〃	CH_3	〃	〃	$n_D^{24.5}$ 1.6093
71	〃		H	〃	〃	

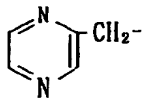
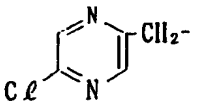
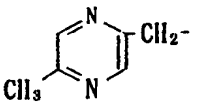
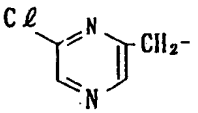
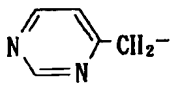
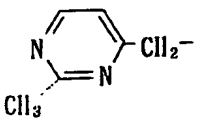
No.	R_1X	R_2	R_3	Z	R_4	[ ] m.p. ℃
72			CH_3	N	CN	(112-114)
73	〃	$CH_2CH=CH_2$	H	〃	〃	n_D^{25} 1.5841
74	〃	〃	CH_3	〃	〃	n_D^{25} 1.5809
75	〃	$CH_2C=CH$	H	〃	〃	
76	〃	〃	CH_3	〃	〃	$n_D^{25.5}$ 1.5730
77	〃	CH_2CN	H	〃	〃	
78	〃	〃	CH_3	〃	〃	(127-128)
79	〃		H	〃	〃	
80	〃	〃	CH_3	〃	〃	(124-127)
81	〃		H	〃	〃	
82	〃	〃	CH_3	〃	〃	$n_D^{24.5}$ 1.6045
83	〃		H	〃	〃	
84	〃	〃	CH_3	〃	〃	$n_D^{25.5}$ 1.6092
85	〃		H	〃	〃	

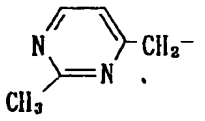
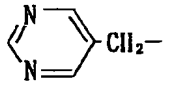
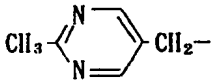
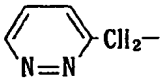
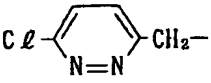
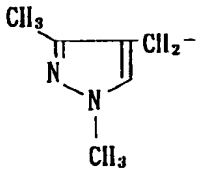
No.	R_1X	R_2	R_3	Z	R_4	[ ] m.p.℃
86			CH_3	N	CN	$n_D^{25.5}$ 1.5910
87	〃		H	〃	〃	
88	〃	〃	CH_3	〃	〃	$n_D^{25.5}$ 1.6162
89	〃		H	〃	〃	
90	〃	〃	CH_3	〃	〃	[115-117]
91	〃	OCH_3	H	〃	〃	
92	〃	〃	CH_3	〃	〃	[110-112]
93	〃	CHO	H	〃	〃	
94	〃	〃	CH_3	〃	〃	
95	〃	$COCH_3$	H	〃	〃	$n_D^{25.5}$ 1.5475
96	〃	〃	CH_3	〃	〃	[84- 86]
97	〃	SO_2CH_3	H	〃	〃	[160-163]
98	〃	〃	CH_3	〃	〃	
99	〃		H	〃	〃	
100	〃	〃	CH_3	〃	〃	[112-114]

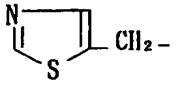
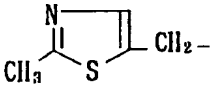
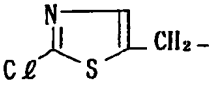
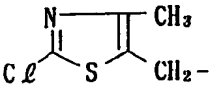
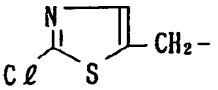
No.	R_1X	R_2	R_3	Z	R_4	[ ] m.p.℃
101		$COOC_2H_5$	H	N	CN	
102	〃	〃	CH_3	〃	〃	n_D^{25} 1.5540
103	〃	$CONH_2$	H	〃	〃	
104	〃	〃	CH_3	〃	〃	
105	〃		H	〃	〃	
106	〃	〃	CH_3	〃	〃	[89- 91]
107	〃	$CONHCH_3$	H	〃	〃	
108	〃	〃	CH_3	〃	〃	
109	〃	$CSNHCH_3$	H	〃	〃	
110	〃	〃	CH_3	〃	〃	
111		H	CH_3	〃	〃	
112	〃	CH_3	〃	〃	〃	
113		H	〃	〃	〃	
114	〃	CH_3	〃	〃	〃	
115		H	〃	〃	〃	[83- 85]

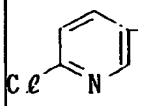
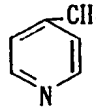
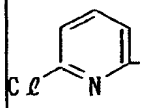
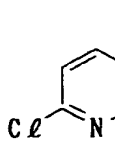
No.	R_1X	R_2	R_3	Z	R_4	[ ] m.p.℃
116		CH_3	CH_3	N	CN	[76- 78]
117		H	〃	〃	〃	
118	〃	CH_3	〃	〃	〃	[145-147]
119		H	〃	〃	〃	
120	〃	CH_3	〃	〃	〃	n_D^{25} 1.5202
121		H	〃	〃	〃	
122	〃	CH_3	〃	〃	〃	
123		H	〃	〃	〃	
124	〃	CH_3	〃	〃	〃	$n_D^{25.5}$ 1.5580
125		H	〃	〃	〃	
126	〃	CH_3	〃	〃	〃	
127		H	〃	〃	〃	
128	〃	CH_3	〃	〃	〃	
129		H	〃	〃	〃	[162-163]
130	〃	CH_3	〃	〃	〃	[105-107]

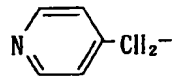
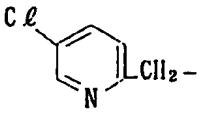
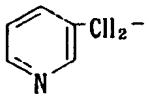
No.	R_1X	R_2	R_3	Z	R_4	[ ] m.p.℃
131		H	CH_3	N	CN	
132	〃	CH_3	〃	〃	〃	[138-139]
133		H	〃	〃	〃	
134	〃	CH_3	〃	〃	〃	n_D^{25} 1.5841
135		H	〃	〃	〃	
136	〃	CH_3	〃	〃	〃	[107-109]
137		H	〃	〃	〃	
138	〃	CH_3	〃	〃	〃	
139		H	〃	〃	〃	
140	〃	CH_3	〃	〃	〃	
141		H	〃	〃	〃	
142	〃	CH_3	〃	〃	〃	
143		H	〃	〃	〃	[122-124]
144	〃	CH_3	〃	〃	〃	[110-113]

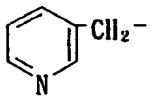
No.	R_1X	R_2	R_3	Z	R_4	( ) m.p.℃
145		H	CH_3	N	CN	(66- 68)
146	〃	CH_3	〃	〃	〃	$n_D^{24.5}$ 1.5790
147		H	〃	〃	〃	
148	〃	CH_3	〃	〃	〃	(94- 96)
149		H	〃	〃	〃	(130-132)
150	〃	CH_3	〃	〃	〃	n_D^{25} 1.5612
151		H	〃	〃	〃	(96- 99)
152	〃	CH_3	〃	〃	〃	$n_D^{25.5}$ 1.5800
153		H	〃	〃	〃	
154	〃	CH_3	〃	〃	〃	
155		H	〃	〃	〃	

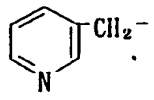
No.	R_1X	R_2	R_3	Z	R_4	[ ] m.p.℃
156		CH_3	CH_3	N	CN	
157		H	〃	〃	〃	
158	〃	CH_3	〃	〃	〃	
159		H	〃	〃	〃	
160	〃	CH_3	〃	〃	〃	
161		H	〃	〃	〃	
162	〃	CH_3	〃	〃	〃	
163		H	〃	〃	〃	[115-117]
164	〃	CH_3	〃	〃	〃	n_D^{23} 1.5717
165		H	〃	〃	〃	[104-106]
166	〃	CH_3	〃	〃	〃	

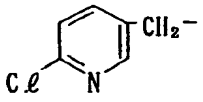
No.	R_1X	R_2	R_3	Z	R_4	( ) m.p.℃
167		H	CH_3	N	CN	
168	〃	CH_3	〃	〃	〃	
169		H	〃	〃	〃	(112-114)
170	〃	CH_3	〃	〃	〃	n_D^{25} 1.5413
171		H	〃	〃	〃	(122-124)
172	〃	CH_3	〃	〃	〃	(143-144)
173	〃	〃	C_2H_5	〃	〃	n_D^{25} 1.5575
174	〃	C_2H_5	CH_3	〃	〃	(63- 70)
175		H	〃	〃	〃	(149-151)
176	〃	CH_3	〃	〃	〃	
177		H	H	〃	〃	(179-183)
178	〃	CH_3	〃	〃	〃	n_D^{25} 1.5952

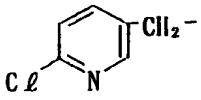
No.	R_1X	R_2	R_3	Z	R_4	[ ] m.p.℃
179		H	CH_3	N	CN	
180	〃	CH_3	〃	〃	〃	
181		H	〃	〃	〃	
182	〃	CH_3	〃	〃	〃	
183		H	〃	〃	〃	
184	〃	CH_3	〃	〃	〃	
185		H	〃	〃	〃	
186	〃	CH_3	〃	〃	〃	
187		H	〃	〃	〃	
188	〃	CH_3	〃	〃	〃	[106-109]
189		H	CH_3	〃	〃	[90- 92]

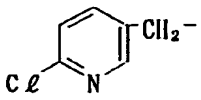
No.	R_1X	R_2	R_3	Z	R_4	[ ] m.p.℃
190		CH_3	CH_3	N	CN	[102-103]
191		H	〃	〃	〃	
192	〃	CH_3	〃	〃	〃	
193		H	H	〃	〃	
194	〃	〃	CH_3	〃	〃	[127-129]
195	〃	〃	$CH_2C\ell$	〃	〃	
196	〃	〃	CH_2F	〃	〃	
197	〃	〃	C_2H_5	〃	〃	
198	〃	〃		〃	〃	
199	〃	〃	CH_2SCH_3	〃	〃	
200	〃	〃	CH_2OCH_3	〃	〃	

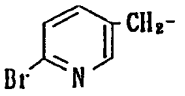
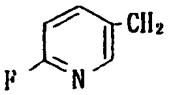
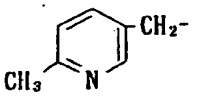
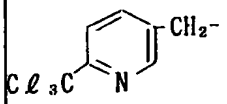
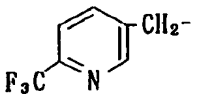
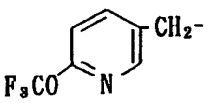
No.	R_1X	R_2	R_3	Z	R_4	[ ] m.p. ℃
201		H	$C_3H_7(n)$	N	CN	$n_D^{25.5}$ 1.5528
202	〃	CH_3	H	〃	〃	
203	〃	〃	CH_3	〃	〃	$n_D^{25.5}$ 1.5798
204	〃	〃	$CH_2C\ell$	〃	〃	
205	〃	〃	CH_2F	〃	〃	
206	〃	H	C_2H_5	〃	〃	$n_D^{25.5}$ 1.5657
207	〃	〃		〃	〃	
208	〃	〃	CH_2SCH_3	〃	〃	
209	〃	〃	CH_2OCH_3	〃	〃	
210	〃	〃	$C_3H_7(i)$	〃	〃	
211	〃	〃	$C_4H_9(t)$	〃	〃	

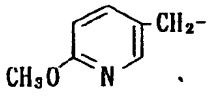
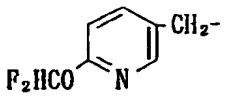
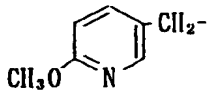
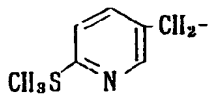
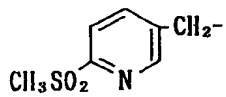
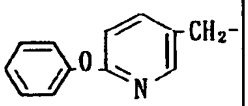
No.	R_1X	R_2	R_3	Z	R_4	[ ] m.p.℃
212		C_2H_5	H	N	CN	
213	〃	〃	CH_3	〃	〃	$n_D^{24.5}$ 1.5665
214	〃	〃	$CH_2C\ell$	〃	〃	
215	〃	〃	C_2H_5	〃	〃	
216	〃	$C_3H_7(i)$	H	〃	〃	
217	〃	〃	CH_3	〃	〃	
218	〃	〃	C_2H_5	〃	〃	
219	〃	$COCH_3$	H	〃	〃	
220	〃	〃	CH_3	〃	〃	
221	〃	SO_2CH_3	H	〃	〃	
222	〃	〃	CH_3	〃	〃	

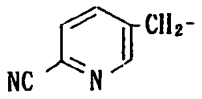
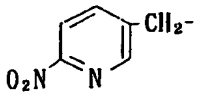
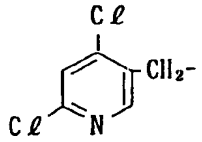
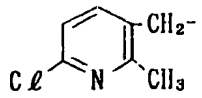
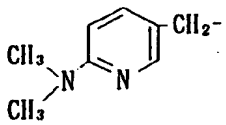
No.	R_1X	R_2	R_3	Z	R_4	[ ] m.p.℃
223		H	H	N	NO_2	
224	〃	〃	CH_3	〃	〃	
225	〃	〃	$CH_2C\ell$	〃	〃	
226	〃	〃	CH_2F	〃	〃	
227	〃	〃	C_2H_5	〃	〃	
228	〃	〃		〃	〃	
229	〃	〃	CH_2SCH_3	〃	〃	
230	〃	〃	CH_2OCH_3	〃	〃	
231	〃	〃	$C_3H_7(i)$	〃	〃	
232	〃	〃	$C_4H_9(t)$	〃	〃	
233	〃	〃	$CH=CH_2$	〃	〃	
234	〃	〃	CH_2	〃	〃	

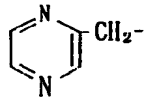
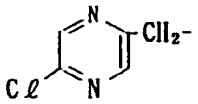
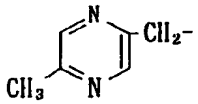
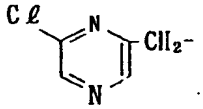
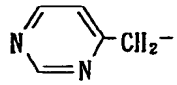
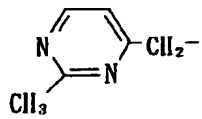
No.	R_1X	R_2	R_3	Z	R_4	[ ] m.p.℃
235		CH_3	H	N	NO_2	
236	〃	〃	CH_3	〃	〃	n_D^{25} 1.5808
237	〃	〃	$CH_2C\ell$	〃	〃	
238	〃	〃	CH_2F	〃	〃	
239	〃	〃	C_2H_5	〃	〃	
240	〃	〃		〃	〃	
241	〃	〃	CH_2SCH_3	〃	〃	
242	〃	〃	CH_2OCH_3	〃	〃	
243	〃	〃	$C_3H_7(n)$	〃	〃	
244	〃	〃	$C_4H_9(t)$	〃	〃	
245	〃	〃	$CH=CH_2$	〃	〃	
246	〃	〃	CH_2	〃	〃	

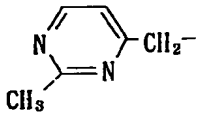
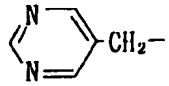
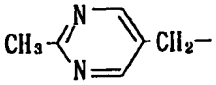
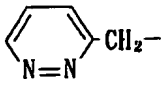
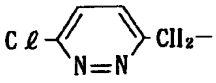
No.	R_1X	R_2	R_3	Z	R_4	[ ] m.p.℃
247		C_2H_5	H	N	NO_2	
248	〃	〃	CH_3	〃	〃	
249	〃	〃	C_2H_5	〃	〃	
250	〃	C_3H_7(i)	H	〃	〃	
251	〃	〃	CH_3	〃	〃	
252	〃	〃	C_2H_5	〃	〃	
253	〃		H	〃	〃	
254	〃	〃	CH_3	〃	〃	
255	〃	〃	C_2H_5	〃	〃	
256	〃	$COCH_3$	H	〃	〃	
257	〃	〃	CH_3	〃	〃	
258	〃	SO_2CH_3	H	〃	〃	
259	〃	〃	CH_3	〃	〃	

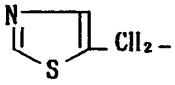
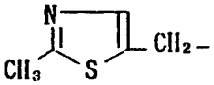
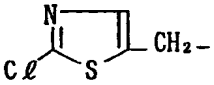
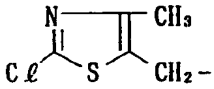
No.	R_1X	R_2	R_3	Z	R_4	( ) m.p.℃
260		H	CH_3	N	NO_2	
261	〃	CH_3	〃	〃	〃	
262		H	〃	〃	〃	
263	〃	CH_3	〃	〃	〃	
264		H	〃	〃	〃	
265	〃	CH_3	〃	〃	〃	
266		H	〃	〃	〃	
267	〃	CH_3	〃	〃	〃	
268		H	〃	〃	〃	
269	〃	CH_3	〃	〃	〃	
270		H	〃	〃	〃	
271	〃	CH_3	〃	〃	〃	

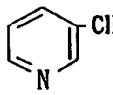
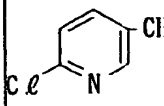
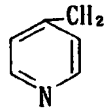
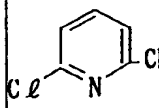
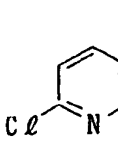
No.	R_1X	R_2	R_3	Z	R_4	[ ] m.p.℃
272		H	CH_3	N	NO_2	
273	〃	CH_3	〃	〃	〃	
274		H	〃	〃	〃	
275	〃	CH_3	〃	〃	〃	
276		H	〃	〃	〃	
277	〃	CH_3	〃	〃	〃	
278		H	〃	〃	〃	
279	〃	CH_3	〃	〃	〃	
280		H	〃	〃	〃	
281	〃	CH_3	〃	〃	〃	
282		H	〃	〃	〃	
283	〃	CH_3	〃	〃	〃	

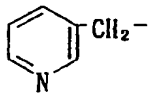
No.	R_1X	R_2	R_3	Z	R_4	[ ] m.p.℃
284		H	CH_3	N	NO_2	
285	〃	CH_3	〃	〃	〃	
286		H	〃	〃	〃	
287	〃	CH_3	〃	〃	〃	
288		H	〃	〃	〃	
289	〃	CH_3	〃	〃	〃	
290		H	〃	〃	〃	
291	〃	CH_3	〃	〃	〃	
292		H	〃	〃	〃	
293	〃	CH_3	〃	〃	〃	

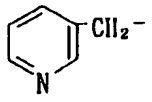
No.	R_1X	R_2	R_3	Z	R_4	[ ] m.p.℃
294		H	CH_3	N	NO_2	
295	〃	CH_3	〃	〃	〃	
296		H	〃	〃	〃	
297	〃	CH_3	〃	〃	〃	
298		H	〃	〃	〃	
299	〃	CH_3	〃	〃	〃	
300		H	〃	〃	〃	
301	〃	CH_3	〃	〃	〃	
302		H	〃	〃	〃	
303	〃	CH_3	〃	〃	〃	
304		H	〃	〃	〃	

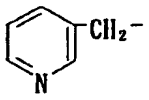
No.	R_1X	R_2	R_3	Z	R_4	[ ] m.p.℃
305		CH_3	CH_3	N	NO_2	
306		H	〃	〃	〃	
307	〃	CH_3	〃	〃	〃	
308		H	〃	〃	〃	
309	〃	CH_3	〃	〃	〃	
310		H	〃	〃	〃	
311	〃	CH_3	〃	〃	〃	
312		H	〃	〃	〃	
313	〃	CH_3	〃	〃	〃	

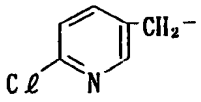
No.	R_1X	R_2	R_3	Z	R_4	[ ] m.p. ℃
314		H	CH_3	N	NO_2	
315	〃	CH_3	〃	〃	〃	
316		H	〃	〃	〃	
317	〃	CH_3	〃	〃	〃	
318		H	〃	〃	〃	
319	〃	CH_3	〃	〃	〃	
320	〃	〃	C_2H_5	〃	〃	
321	〃	C_2H_5	CH_3	〃	〃	
322		H	〃	〃	〃	
323	〃	CH_3	〃	〃	〃	

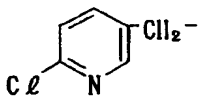
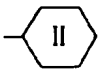
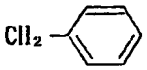
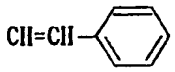
No.	R_1X	R_2	R_3	Z	R_4	[ ] m.p.℃
324		H	CH_3	N	NO_2	
325	〃	CH_3	〃	〃	〃	
326		H	〃	〃	〃	
327	〃	CH_3	〃	〃	〃	
328		H	〃	〃	〃	
329	〃	CH_3	〃	〃	〃	
330		H	〃	〃	〃	
331	〃	CH_3	〃	〃	〃	
332		H	〃	〃	〃	
333	〃	CH_3	〃	〃	〃	
334		H	〃	〃	〃	
335	〃	CH_3	〃	〃	〃	

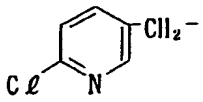
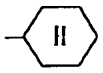
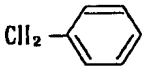
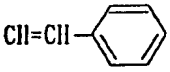
No.	R_1X	R_2	R_3	Z	R_4	[ ] m.p.℃
336		H	H	N	NO_2	
337	〃	〃	CH_3	〃	〃	
338	〃	〃	C_2H_5	〃	〃	
339	〃	〃	$CH_2C\ell$	〃	〃	
340	〃	〃	CH_2F	〃	〃	
341	〃	〃		〃	〃	
342	〃	〃	CH_2SCH_3	〃	〃	
343	〃	〃	CH_2OCH_3	〃	〃	

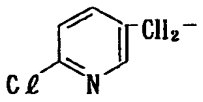
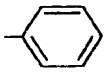
No.	R_1X	R_2	R_3	Z	R_4	( ) m.p. ℃
344		CH_3	H	N	NO_2	
345	〃	〃	CH_3	〃	〃	
346	〃	〃	$CH_2C\ell$	〃	〃	
347	〃	〃	CH_2F	〃	〃	
348	〃	〃	C_2H_5	〃	〃	
349	〃	〃		〃	〃	
350	〃	〃	CH_2SCH_3	〃	〃	
351	〃	〃	CH_2OCH_3	〃	〃	
352	〃	〃	$C_3H_7(i)$	〃	〃	
353	〃	〃	$C_4H_9(t)$	〃	〃	

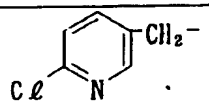
No.	R_1X	R_2	R_3	Z	R_4	[ ] m.p.℃
354		C_2H_5	H	N	NO_2	
355	〃	〃	CH_3	〃	〃	
356	〃	〃	$CH_2C\ell$	〃	〃	
357	〃	〃	C_2H_5	〃	〃	
358	〃	$C_3H_7(i)$	H	〃	〃	
359	〃	〃	CH_3	〃	〃	
360	〃	〃	C_2H_5	〃	〃	
361	〃	$COCH_3$	H	〃	〃	
362	〃	〃	CH_3	〃	〃	
363	〃	SO_2CH_3	H	〃	〃	
364	〃	〃	CH_3	〃	〃	

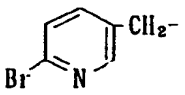
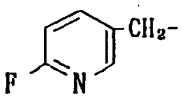
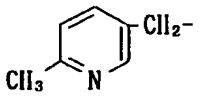
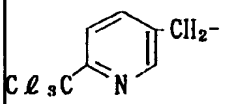
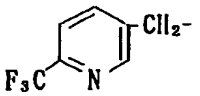
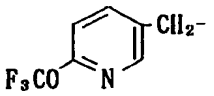
No.	R_1X	R_2	R_3	Z	R_4	[ ] m.p.℃
365		H	H	CH	NO_2	[116-118]
366	〃	〃	CH_3	〃	〃	[133-135]
367	〃	〃	$CH_2C\ell$	〃	〃	
368	〃	〃	C_2H_5	〃	〃	[95- 98]
369	〃	〃	C_3H_7(i)	〃	〃	[150-152]
370	〃	〃	C_3H_7(t)	〃	〃	
371	〃	〃	$CH=CH_2$	〃	〃	
372	〃	〃	$CH=CHCH_3$	〃	〃	
373	〃	〃	CH_2CN	〃	〃	
374	〃	〃	CH_2NO_2	〃	〃	
375	〃	〃	$CH_2COOC_2H_5$	〃	〃	

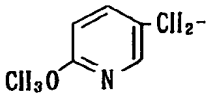
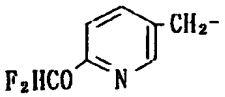
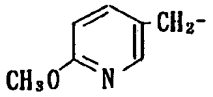
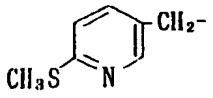
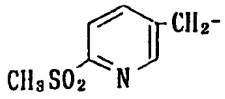
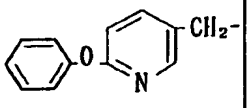
No.	R_1X	R_2	R_3	Z	R_4	( ) m.p.℃
376		H		CH	NO_2	
377	〃	〃		〃	〃	
378	〃	〃		〃	〃	
379	〃	〃		〃	〃	
380	〃	CH_3	H	〃	〃	
381	〃	〃	CH_3	〃	〃	〔 79- 82 〕
382	〃	〃	$CH_2C\ell$	〃	〃	
383	〃	〃	C_2H_5	〃	〃	〔101-104 〕
384	〃	〃	C_3H_7(i)	〃	〃	
385	〃	〃	C_4H_7(t)	〃	〃	
386	〃	〃	$CH=CH_2$	〃	〃	
387	〃	〃	$CH=CHCH_3$	〃	〃	

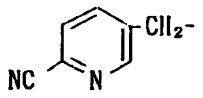
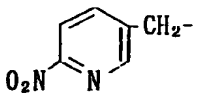
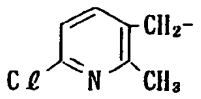
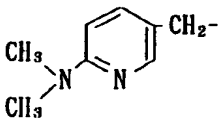
No.	R_1X	R_2	R_3	Z	R_4	[ ] m.p.℃
388		CH_3	CH_2CN	CH	NO_2	
389	〃	〃	CH_2NO_2	〃	〃	
390	〃	〃	$CH_2COOC_2H_5$	〃	〃	
391	〃	〃		〃	〃	
392	〃	〃		〃	〃	
393	〃	〃		〃	〃	
394	〃	〃		〃	〃	
395	〃	C_2H_5	H	〃	〃	
396	〃	〃	CH_3	〃	〃	
397	〃	〃	C_2H_5	〃	〃	
398	〃	$C_3H_7(i)$	H	〃	〃	
399	〃	〃	CH_3	〃	〃	

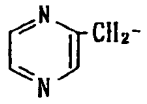
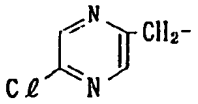
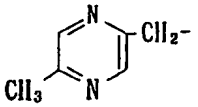
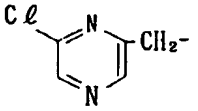
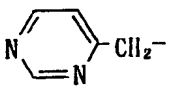
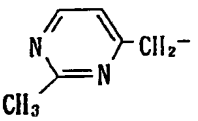
No.	R_1X	R_2	R_3	Z	R_4	[ ] m.p.℃
400		$C_3H_7(i)$	C_2H_5	CH	NO_2	
401	〃		H	〃	〃	
402	〃	〃	CH_3	〃	〃	
403	〃	〃	C_2H_5	〃	〃	
404	〃	$CH_2CH=CH_2$	H	〃	〃	
405	〃	〃	CH_3	〃	〃	
406	〃	〃	C_2H_5	〃	〃	
407	〃		H	〃	〃	
408	〃	〃	CH_3	〃	〃	
409	〃	〃	C_2H_5	〃	〃	
410	〃	CHO	H	〃	〃	
411	〃	〃	CH_3	〃	〃	

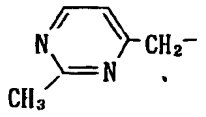
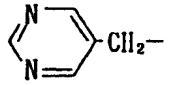
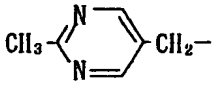
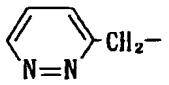
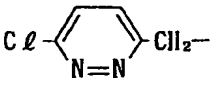
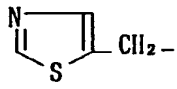
No.	R_1X	R_2	R_3	Z	R_4	( ) m.p.℃
412		CHO	C_2H_5	CH	NO_2	
413	〃	$COCH_3$	H	〃	〃	
414	〃	〃	CH_3	〃	〃	
415	〃	〃	C_2H_5	〃	〃	
416	〃	SO_2CH_3	H	〃	〃	
417	〃	〃	CH_3	〃	〃	
418	〃	〃	C_2H_5	〃	〃	
419	〃	$COOC_2H_5$	H	〃	〃	
420	〃	〃	CH_3	〃	〃	
421	〃	〃	C_2H_5	〃	〃	
422	〃	OC_2H_5	H	〃	〃	
423	〃	〃	CH_3	〃	〃	
424	〃	〃	C_2H_5	〃	〃	
425	〃	$CH_2C=CH$	H	〃	〃	
426	〃	〃	CH_3	〃	〃	
427	〃	〃	C_2H_5	〃	〃	

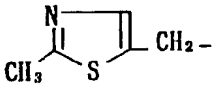
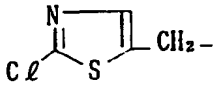
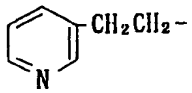
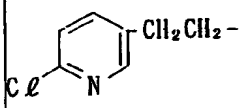
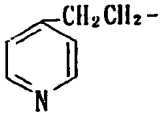
No.	R_1X	R_2	R_3	Z	R_4	[ ] m.p.℃
428		H	CH_3	CH	NO_2	
429	〃	CH_3	〃	〃	〃	
430		H	〃	〃	〃	
431	〃	CH_3	〃	〃	〃	
432		H	〃	〃	〃	
433	〃	CH_3	〃	〃	〃	
434		H	〃	〃	〃	
435	〃	CH_3	〃	〃	〃	
436		H	〃	〃	〃	
437	〃	CH_3	〃	〃	〃	
438		H	〃	〃	〃	
439	〃	CH_3	〃	〃	〃	

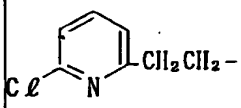
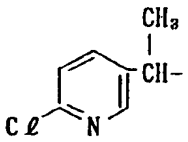
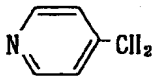
No.	R_1X	R_2	R_3	Z	R_4	[ ] m.p.℃
440		H	CH_3	CH	NO_2	
441	〃	CH_3	〃	〃	〃	
442		H	〃	〃	〃	
443	〃	CH_3	〃	〃	〃	
444		H	〃	〃	〃	
445	〃	CH_3	〃	〃	〃	
446		H	〃	〃	〃	
447	〃	CH_3	〃	〃	〃	
448		H	〃	〃	〃	
449	〃	CH_3	〃	〃	〃	
450		H	〃	〃	〃	
451	〃	CH_3	〃	〃	〃	

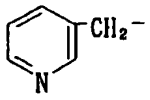
No.	R_1X	R_2	R_3	Z	R_4	[ ] m.p.℃
452		H	CH_3	CH	NO_2	
453	〃	CH_3	〃	〃	〃	
454		H	〃	〃	〃	
455	〃	CH_3	〃	〃	〃	
456		H	〃	〃	〃	
457	〃	CH_3	〃	〃	〃	
458		H	〃	〃	〃	
459	〃	CH_3	〃	〃	〃	
460		H	〃	〃	〃	
461	〃	CH_3	〃	〃	〃	

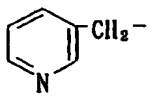
No.	R_1X	R_2	R_3	Z	R_4	[ ] m.p.℃
462		H	CH_3	CH	NO_2	
463	〃	CH_3	〃	〃	〃	
464		H	〃	〃	〃	
465	〃	CH_3	〃	〃	〃	
466		H	〃	〃	〃	
467	〃	CH_3	〃	〃	〃	
468		H	〃	〃	〃	
469	〃	CH_3	〃	〃	〃	
470		H	〃	〃	〃	
471	〃	CH_3	〃	〃	〃	
472		H	〃	〃	〃	

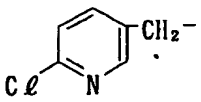
No.	R_1X	R_2	R_3	Z	R_4	[ ] m.p. ℃
473		CH_3	CH_3	CH	NO_2	
474		H	〃	〃	〃	
475	〃	CH_3	〃	〃	〃	
476		H	〃	〃	〃	
477	〃	CH_3	〃	〃	〃	
478		H	〃	〃	〃	
479	〃	CH_3	〃	〃	〃	
480		H	〃	〃	〃	
481	〃	CH_3	〃	〃	〃	
482		H	〃	〃	〃	
483	〃	CH_3	〃	〃	〃	

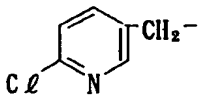
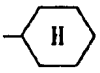
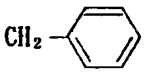
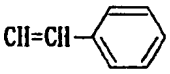
No.	R_1X	R_2	R_3	Z	R_4	[ ] m.p.℃
484		H	CH_3	CH	NO_2	
485	〃	CH_3	〃	〃	〃	
486		H	〃	〃	〃	
487	〃	CH_3	〃	〃	〃	
488	〃	〃	C_2H_5	〃	〃	
489	〃	C_2H_5	CH_3	〃	〃	
490		H	〃	〃	〃	
491	〃	CH_3	〃	〃	〃	
492		H	〃	〃	〃	
493	〃	CH_3	〃	〃	〃	
494		H	〃	〃	〃	
495	〃	CH_3	〃	〃	〃	

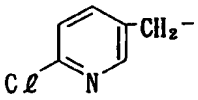
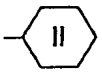
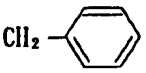
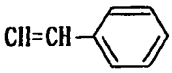
No.	R_1X	R_2	R_3	Z	R_4	[ ] m.p.℃
496		H	CH_3	CH	NO_2	
497	〃	CH_3	〃	〃	〃	
498		H	〃	〃	〃	
499	〃	CH_3	〃	〃	〃	
500		H	〃	〃	〃	
501	〃	CH_3	〃	〃	〃	

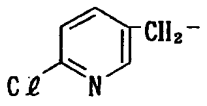
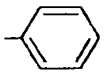
No.	R_1X	R_2	R_3	Z	R_4	( ) m.p.℃
502		H	H	CH	NO_2	
503	〃	〃	CH_3	〃	〃	
504	〃	〃	$CH_2C\ell$	〃	〃	
505	〃	〃	C_2H_5	〃	〃	
506	〃	〃	$C_3H_7(i)$	〃	〃	
507	〃	〃	$C_4H_9(t)$	〃	〃	
508	〃	CH_3	H	〃	〃	
509	〃	〃	CH_3	〃	〃	
510	〃	〃	$CH_2C\ell$	〃	〃	
511	〃	〃	C_2H_5	〃	〃	
512	〃	〃		〃	〃	

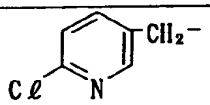
No.	R_1X	R_2	R_3	Z	R_4	[ ] m.p.℃
513		CH_3	C_3H_7(i)	CH	NO_2	
514	〃	〃	C_4H_9(t)	〃	〃	
515	〃	C_2H_5	H	〃	〃	
516	〃	〃	CH_3	〃	〃	
517	〃	〃	C_2H_5	〃	〃	
518	〃		H	〃	〃	
519	〃	〃	CH_3	〃	〃	
520	〃	〃	C_2H_5	〃	〃	
521	〃	$COCH_3$	H	〃	〃	
522	〃	〃	CH_3	〃	〃	
523	〃	〃	C_2H_5	〃	〃	
524	〃	SO_2CH_3	H	〃	〃	
525	〃	〃	CH_3	〃	〃	
526	〃	〃	C_2H_5	〃	〃	

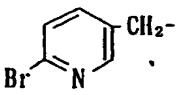
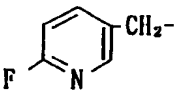
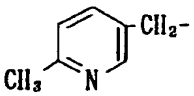
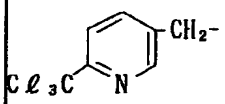
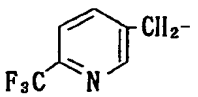
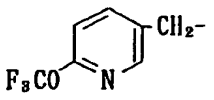
No.	R_1X	R_2	R_3	Z	R_4	( ) m.p.℃
527		H	H	CH	CN	
528	〃	〃	CH_3	〃	〃	(95- 98)
529	〃	〃	$CH_2C\ell$	〃	〃	
530	〃	〃	C_2H_5	〃	〃	
531	〃	〃	$C_3H_7(i)$	〃	〃	
532	〃	〃	$C_4H_9(t)$	〃	〃	
533	〃	〃	$CH=CH_2$	〃	〃	
534	〃	〃	$CH=CHCH_3$	〃	〃	
535	〃	〃	CH_2CN	〃	〃	
536	〃	〃	CH_2NO_2	〃	〃	
537	〃	〃	$CH_2COOC_2H_5$	〃	〃	

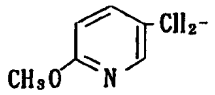
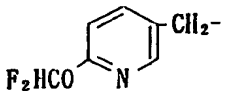
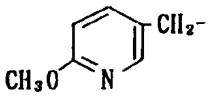
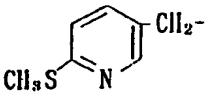
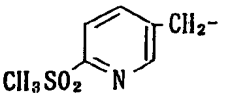
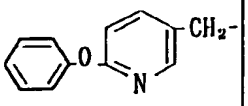
No.	R_1X	R_2	R_3	Z	R_4	[ ] m.p.℃
538		H		CH	CN	
539	〃	〃		〃	〃	
540	〃	〃		〃	〃	
541	〃	〃		〃	〃	
542	〃	CH_3	H	〃	〃	
543	〃	〃	CH_3	〃	〃	n_D^{29} 1.5941
544	〃	〃	$CH_2C\ell$	〃	〃	
545	〃	〃	C_2H_5	〃	〃	
546	〃	〃	C_3H_7(i)	〃	〃	
547	〃	〃	C_4H_9(t)	〃	〃	
548	〃	〃	$CH=CH_2$	〃	〃	
549	〃	〃	$CH=CHCH_3$	〃	〃	

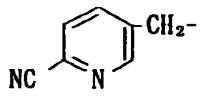
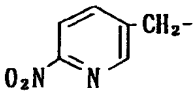
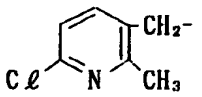
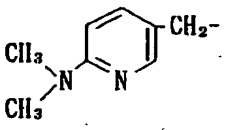
No.	R_1X	R_2	R_3	Z	R_4	[ ] m.p.℃
550		CH_3	CH_2CN	CH	CN	
551	〃	〃	CH_2NO_2	〃	〃	
552	〃	〃	$CH_2COOC_2H_5$	〃	〃	
553	〃	〃		〃	〃	
554	〃	〃		〃	〃	
555	〃	〃		〃	〃	
556	〃	〃		〃	〃	
557	〃	C_2H_5	H	〃	〃	
558	〃	〃	CH_3	〃	〃	
559	〃	〃	C_2H_5	〃	〃	
560	〃	C_3H_7(i)	H	〃	〃	
561	〃	〃	CH_3	〃	〃	

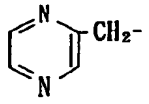
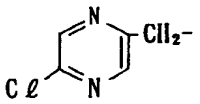
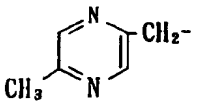
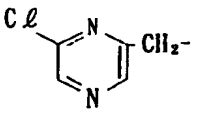
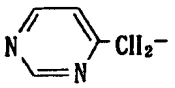
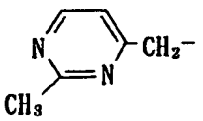
No.	R_1X	R_2	R_3	Z	R_4	[ ] m.p.℃
562		C_3H_7(i)	C_2H_5	CH	CN	
563	〃		H	〃	〃	
564	〃	〃	CH_3	〃	〃	
565	〃	〃	C_2H_5	〃	〃	
566	〃	$CH_2CH=CH_2$	H	〃	〃	
567	〃	〃	CH_3	〃	〃	
568	〃	〃	C_2H_5	〃	〃	
569	〃		H	〃	〃	
570	〃	〃	CH_3	〃	〃	
571	〃	〃	C_2H_5	〃	〃	
572	〃	CHO	H	〃	〃	
573	〃	〃	CH_3	〃	〃	

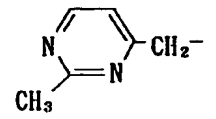
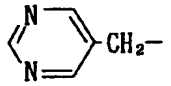
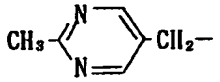
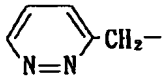
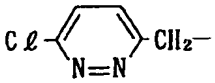
No.	R_1X	R_2	R_3	Z	R_4	[ ] m.p.℃
574		CHO	C_2H_5	CH	CN	
575	〃	$COCH_3$	H	〃	〃	
576	〃	〃	CH_3	〃	〃	
577	〃	〃	C_2H_5	〃	〃	
578	〃	SO_2CH_3	H	〃	〃	
579	〃	〃	CH_3	〃	〃	
580	〃	〃	C_2H_5	〃	〃	
581	〃	$COOC_2H_5$	H	〃	〃	
582	〃	〃	CH_3	〃	〃	
583	〃	〃	C_2H_5	〃	〃	
584	〃	OC_2H_5	H	〃	〃	
585	〃	〃	CH_3	〃	〃	
586	〃	〃	C_2H_5	〃	〃	
587	〃	$CH_2C=CH$	H	〃	〃	
588	〃	〃	CH_3	〃	〃	
589	〃	〃	C_2H_5	〃	〃	

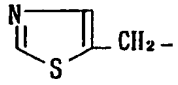
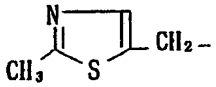
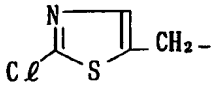
No.	R_1X	R_2	R_3	Z	R_4	[ ] m.p. ℃
590		H	CH_3	CH	CN	
591	〃	CH_3	〃	〃	〃	
592		H	〃	〃	〃	
593	〃	CH_3	〃	〃	〃	
594		H	〃	〃	〃	
595	〃	CH_3	〃	〃	〃	
596		H	〃	〃	〃	
597	〃	CH_3	〃	〃	〃	
598		H	〃	〃	〃	
599	〃	CH_3	〃	〃	〃	
600		H	〃	〃	〃	
601	〃	CH_3	〃	〃	〃	

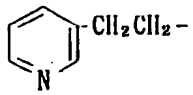
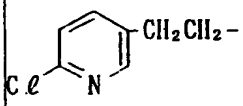
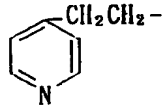
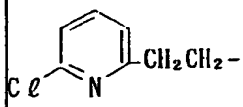
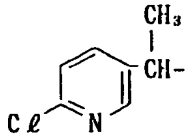
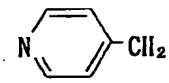
No.	R_1X	R_2	R_3	Z	R_4	[ ] m.p.℃
602		H	CH_3	CH	CN	
603	〃	CH_3	〃	〃	〃	
604		H	〃	〃	〃	
605	〃	CH_3	〃	〃	〃	
606		H	〃	〃	〃	
607	〃	CH_3	〃	〃	〃	
608		H	〃	〃	〃	
609	〃	CH_3	〃	〃	〃	
610		H	〃	〃	〃	
611	〃	CH_3	〃	〃	〃	
612		H	〃	〃	〃	
613	〃	CH_3	〃	〃	〃	

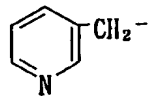
No.	R_1X	R_2	R_3	Z	R_4	[ ] m.p.℃
614		H	CH_3	CH	CN	
615	〃	CH_3	〃	〃	〃	
616		H	〃	〃	〃	
617	〃	CH_3	〃	〃	〃	
618		H	〃	〃	〃	
619	〃	CH_3	〃	〃	〃	
620		H	〃	〃	〃	
621	〃	CH_3	〃	〃	〃	
622		H	〃	〃	〃	
623	〃	CH_3	〃	〃	〃	

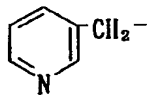
No.	R_1X	R_2	R_3	Z	R_4	[ ] m.p.℃
624		H	CH_3	CH	CN	
625	〃	CH_3	〃	〃	〃	
626		H	〃	〃	〃	
627	〃	CH_3	〃	〃	〃	
628		H	〃	〃	〃	
629	〃	CH_3	〃	〃	〃	
630		H	〃	〃	〃	
631	〃	CH_3	〃	〃	〃	
632		H	〃	〃	〃	
633	〃	CH_3	〃	〃	〃	
634		H	〃	〃	〃	

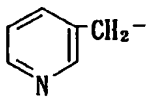
No.	R_1X	R_2	R_3	Z	R_4	[ ] m.p.℃
635		CH_3	CH_3	CH	CN	
636		H	〃	〃	〃	
637	〃	CH_3	〃	〃	〃	
638		H	〃	〃	〃	
639	〃	CH_3	〃	〃	〃	
640		H	〃	〃	〃	
641	〃	CH_3	〃	〃	〃	
642		H	〃	〃	〃	
643	〃	CH_3	〃	〃	〃	

No.	R_1X	R_2	R_3	Z	R_4	[ ] m.p.℃
644		H	CH_3	CH	CN	
645	〃	CH_3	〃	〃	〃	
646		H	〃	〃	〃	
647	〃	CH_3	〃	〃	〃	
648		H	〃	〃	〃	
649	〃	CH_3	〃	〃	〃	
650	〃	〃	C_2H_5	〃	〃	
651	〃	C_2H_5	CH_3	〃	〃	

No.	R_1X	R_2	R_3	Z	R_4	[ ] m.p.℃
652		H	CH_3	CH	CN	
653	〃	CH_3	〃	〃	〃	
654		H	〃	〃	〃	
655	〃	CH_3	〃	〃	〃	
656		H	〃	〃	〃	
657	〃	CH_3	〃	〃	〃	
658		H	〃	〃	〃	
659	〃	CH_3	〃	〃	〃	
660		H	〃	〃	〃	
661	〃	CH_3	〃	〃	〃	
662		H	〃	〃	〃	
663	〃	CH_3	〃	〃	〃	

No.	R_1X	R_2	R_3	Z	R_4	( ) m.p.℃
664		H	H	CH	CN	
665	〃	〃	CH_3	〃	〃	
666	〃	〃	$CH_2C\ell$	〃	〃	
667	〃	〃	C_2H_5	〃	〃	
668	〃	〃	$C_3H_7(i)$	〃	〃	
669	〃	〃	$C_4H_9(t)$	〃	〃	
670	〃	CH_3	H	〃	〃	
671	〃	〃	CH_3	〃	〃	
672	〃	〃	$CH_2C\ell$	〃	〃	
673	〃	〃	C_2H_5	〃	〃	
674	〃	〃		〃	〃	

No.	R_1X	R_2	R_3	Z	R_4	[ ] m.p.℃
675		CH_3	C_3H_7(i)	CH	CN	
676	〃	〃	C_4H_9(t)	〃	〃	
677	〃	C_2H_5	H	〃	〃	
678	〃	〃	CH_3	〃	〃	
679	〃	〃	C_2H_5	〃	〃	
680	〃		H	〃	〃	
681	〃	〃	CH_3	〃	〃	
682	〃	〃	C_2H_5	〃	〃	
683	〃	$COCH_3$	H	〃	〃	
684	〃	〃	CH_3	〃	〃	
685	〃	〃	C_2H_5	〃	〃	
686	〃	SO_2CH_3	H	〃	〃	

No.	R_1X	R_2	R_3	Z	R_4	[ ] m.p.℃
687		SO_2CH_3	CH_3	CH	CN	
688	〃	〃	C_2H_5	〃	〃	

* 1
^{1}H-NMR($CDCl_3$) δ ;ppm 3.32 (s, 3H), 4.63 (s, 2H), 7.37 (d, 1H), 7.62 (dd, 1H), 8.37 (d, 1H)

The compounds of this invention exhibit high insecticidal activities against various species of insect pests such as cutworms, diamondback moth, aphids, leafhoppers and planthoppers. In recent years the decrease of the control effects of organophosphorus and carbamate insecticides, which is caused by the development of resistance to these insecticides, has become serious problem. In such situations, the development of new insecticides which is effective on the resistant pests has been desired. The compounds of this invention possess superior insecticidal activities against not only susceptible strains but also resistant ones.

The insecticides covered by this invention contain as active ingredients one or more types of the compounds as expressed by the general formula (1). These active ingredients, may be used as-produced but normally they are used in any of the forms which ordinary agricultural chemicals can take, namely wettable powder, dust, emulsifiable concentrate, suspension concentrates, smoking chemicals, fumigant, granule, or other formulations. For additives and carriers are used soybean flour, wheat flour or other vegetable flours, diatomaceous earth, apatite, gypsum, talc, pyrophyllite, clay or other fine mineral powders, when solid formulations are intended.

When liquid formulations are intended, then for solvents are used kerosene, mineral oil, petroleum, solvent naphtha, xylene, cyclohexane, cyclohexanone, dimethylformamide, dimethylsulfoxide, alcohol, acetone, water, etc. A surface active agent may, if necessary, be added in order to give a homogeneous and suitable formulation. The wettable powders, emulsifiable concentrates,

suspension concentrates, etc. thus obtained are diluted with water into suspensions or emulsions of a prescribed concentration, before they are actually sprayed on plants in the field. In the case of dusts or granules, they are directly applied without further processing.

It goes without saying that the compound(s) of this invention is effective even alone, but it can be used by mixing with various types of insecticides, acaricides and fungicides.

Typical examples of acaricides and insecticides which can be used by mixing with the compounds of this invention are described below:

Acaricides (fungicides):

chlorobenzilate, chloropropylate, proclonol, bromopropylate, dicofol, dinobuton, binapacryl, chlordimeform, amitraz, propargite, PPPS, benzoximate, hexythiazox, fenbutatin oxide, polynactine, chinomethionat, thioquinox, chlorfenson, tetradifon, phenproxide, avermectins, clofentezine, flubenzimine, fenazaquin, pyridaben, fenproximate, chlorfenethol, thiophanate-methyl, benomyl, thiram, iprobenfos, edifenfos, fthalide, probenazole, isoprothiolane, chorothalonil, captan, polyoxin-B, blasticidin-S, kasugamycin, validamycin, tricyclazole, pyroquilon, phenazine oxide, mepronil, flutolanil, pencycuron, iprodione, hymexazole, metalaxyl, triflumizole, diclomezine, tecloftalam, vinclozolin, procymidone, bitertanol, triadimefon, prochloraz, pyrifenox, fenarimal, fenpropimorph, triforine, metalaxyl, oxycarboxin, pefrazoate, diclomedine, fluazinam, oxadixyl, ethoquinolac, TPTH, propamocarb, fosetyl, dihydrostreptomycin, anilazine, dithianon, diethofencarb.

Organophosphorus-type and carbamate-type insecticides(acaridides):

fenthion, fenitrothion, diazinon, chlorpyrifos, oxydeprofos, vamidothion, phenthoate, dimethoate, formothion, malathion, trichlorfon, thiometon, phosmet, menazon, dichlorvos, acephate, EPBP, dialifos, parathion-methyl, oxydemeton-methyl, ethion, aldicarb, propoxur, methomyl, fenobucarb, BPMC, pyraclofos, monocrotophos, salithion, cartap, carbosulfan carbofuran, benfuracarb, metolcarb, carbaryl, pirimicarb, ethiofencarb, fenoxycarb,

Pyrethroide-type insecticides (acaricides):

permethrin, cypermethrin, deltamethrin, fenvalerate, fenpropathrin, pyrethrins, allethrin, tetramethrin, resmethrin, parthrin, dimethrin, proparthrin, bifenthrin, prothrin, fluvalinate, cyfluthrin, cyhalothrin, flucythrinate, ethofenprox, cycloprothrin, tralomethrin, silaneophan.

Benzoylphenylurea-type and other types insecticides:

diflubenzuron, chlorfluazuron, triflumuron, teflubenzuron, buprofezin, pyriproxyfen, flufenoxuron, Machine oil.

Same examples of the formulations are given below. The carriers, surface-active agents, etc. that are added, however, are not limited to these Examples.

Example 7 : Emulsifiable concentrate

The compound of this invention	10 parts
Alkylphenyl polyoxyethylene	5 parts
Dimethyl formamide	50 parts
Xylene	35 parts

These components are mixed and dissolved and, for use in spraying, the liquid mixture is water-diluted into an emulsion.

Example 8 : Wettable powder

The compound of this invention	20 parts
Higher alcohol sulfuric ester	5 parts
Diatomaceous earth	70 parts
Silica	5 parts

These components are mixed and ground to fine powder, which for use in spraying, are water-diluted into a suspension.

Example 9 : Dust

The compound of this invention	5 parts
Talc	94.7 parts
Silica	0.3 parts

These are mixed and ground and used as-ground in spraying.

Example 10 : Granule

The compound of this invention	5 parts
Clay	73 parts
Bentonite	20 parats
Sodium dioctylsulfosuccinate	1 part
Sodium phosphate	1 part

The above compounds are granulated, and applied as it is when used.

Industrial applicability:

The tests below show the insecticidal activity of the compounds of this invention.

Test 1 Efficacy for cotton aphid

30 to 50 insects of cotton aphid per plot were inoculated using a small brush on cucumber leaves which were seeded in pots, 10cm in diameter, and 10 days old after germination. A day later, wounded insect pests were removed, and a chemical solution, which was prepared in the way that the emulsifiable concentrate described in Example 7 of the above example of insecticide was diluted with water to 125 ppm of compound concentration according to the prescription, was sprayed. The pots were placed in a thermostatic room at temperature of 25°C and humidity of 65%. The number of survival pests was counted 7 days later and the control efficacy was calculated by comparing with that of untreated plot. The results are shown in Table 2.

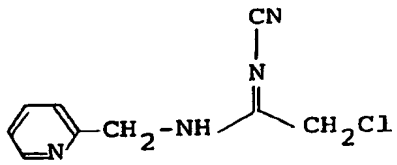
Table 2

Compound No.	Control Efficacy (7 days later) 125 ppm
1	100 %
2	100
3	100
4	100
6	100
8	100
10	100
16	100
20	100
21	100
22	100
23	100
24	100
25	100
27	100
29	100
31	100
32	100
33	100
38	100
44	100
48	100
50	100
51	100
53	100
57	100
60	100
62	100
64	100
66	100
68	100
70	100
72	100

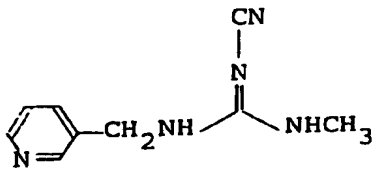
Compound No.	Control Efficacy
73	100
74	100
78	100
80	100
82	100
84	100
86	100
88	100
92	100
96	100
100	100
102	100
115	100
116	100
120	100
124	100
130	100
132	100
136	100
144	100
145	100
146	100
148	100
149	100
150	100
151	100
152	100
163	100
164	100
169	100
170	100
171	100
172	100
173	100
174	100

Compound No.	Control Efficacy
177	100
178	100
188	100
189	100
190	100
194	100
203	100
206	100
213	100
236	100
366	100
368	100
381	100
383	100
543	100
Comparative compound A	27
" B	100

Comparative compound A:



Comparative compound B:



Test 2 Efficacy for green rice leafhopper

Rice seedlings of 7 days old after germination were immersed in a chemical solution, which was prepared in the way that the emulsifiable concentrate described in Example 7 of the above example of insecticide was diluted with water to 125 ppm of compound concentration according to prescription, for 30 seconds. After dried in air, the treated seedlings were placed in test tubes and 10 insects of 3rd-instar larvae of green rice leafhopper resistant to the organophosphorus and carbamate insecticides were inoculated. The tubes were covered with gauze, and placed in a thermostatic room at temperature of 25°C and humidity of 65%. The mortality was checked 5 days later.

The results are shown in Table 3.

Table 3

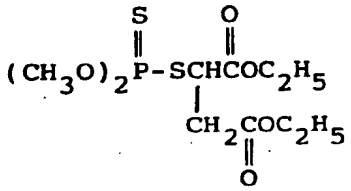
Compound No.	% mortality (5 days later) 125 ppm
1	100 %
2	100
4	100
6	100
8	100
10	100
16	100
18	100
20	100
21	100
22	100
23	100
24	100
25	100
27	100
28	100
29	100
31	100
32	100
33	100
35	100
36	100
44	100
48	100
50	100
51	100
53	100
57	100
60	100
62	100
66	100
68	100
72	100
73	100

Compound No.	% Mortality
74	100
78	100
82	100
84	100
86	100
88	100
92	100
96	100
100	100
102	100
116	100
120	100
124	100
130	100
132	100
136	100
144	100
146	100
148	100
150	100
152	100
164	100
169	100
170	100
171	100
172	100
173	100
174	100
178	100
188	100
190	100
201	100
203	100

Compound No.	% Mortality
213	100
236	100
366	100
368	100
369	100
381	100
Comparative Compound A	0
" B	0
" C	0

Comparative compound A and B: The same as test 1

Compound C:



(malathion)

Test 3 Efficacy for rice armyworm

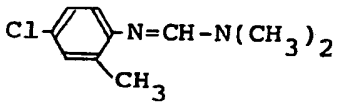
The test compounds were formulated into the wettable powder in the same manner as Example 8. The compounds were diluted with water to 125 ppm. A maize leaf was immersed in the chemical solution for 30 seconds. After air-dried, the treated leaf was placed in a petri dish and five 3rd-instar larvae of rice armyworm were inoculated. The petri dishes were covered with glass lids, and placed in a thermostatic room at 25°C and 65% relative humidity. The mortality was checked 5 days later. Two replications were conducted in the each test. The results are shown in Table 4.

Table 4

Compound No.	% mortality (5 days later) 125 ppm
21	100 %
22	100
23	100
24	100
25	100
51	100
57	100
88	100
92	100
148	100
172	100
381	100
Comparative compound A	0
" B	0
" D	40

Comparative compound A and B: The same as Test 1

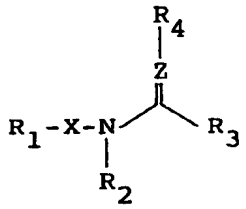
Compound D:



(chlordimeform)

Claims

1. A compound having the formula



wherein R_1 represents an optionally substituted 5 - 6 membered aromatic hetero ring containing nitrogen atom, except a non-substituted 2-pyridyl;

X represents an optionally substituted C_{1-3} alkylene or alkylidene;

R_2 represents a hydrogen, a carbamoyl, a mono or di C_{1-5} alkyl carbamoyl, a thiocarbamoyl, a mono or di C_{1-5} alkylthiocarbamoyl, a sulfamoyl, a mono or di C_{1-5} alkylsulfamoyl, an optionally substituted C_{1-5} alkyl, an optionally substituted C_{2-5} alkenyl, an optionally substituted C_{2-5} alkynyl, an optionally substituted C_{3-8} cycloalkyl, an optionally substituted C_{3-8} cycloalkenyl, an optionally substituted aryl or $-Y-R_5$;

Y represents O, $S(O)_n$, CO, CS or CO_2;

n represents 0,1 or 2;

R_5 represents a hydrogen, an optionally substituted C_{1-5} alkyl, an optionally substituted C_{2-5} alkenyl, an optionally substituted C_{2-5} alkynyl, an optionally substituted C_{3-8} cycloalkyl, an optionally substituted C_{3-8} cycloalkenyl or an optionally substituted aryl;

R_3 represents a hydrogen, an optionally substituted C_{1-5} alkyl, an optionally substituted C_{2-5} alkenyl, an optionally

substituted C_{2-5} alkynyl, an optionally substituted C_{3-8} cycloalkyl or an optionally substituted C_{3-8} cycloalkenyl;

R_4 represents a cyano or a nitro; and Z represents CH or N;

or its salt.

2. A compound according to claim 1,

wherein R_1 represents a pyridyl, a pyrazyl, a pyrazolyl, a pyridazyl or a thiazolyl, which may be substituted by a C_{1-5} alkyl, a C_{1-5} haloalkyl, a C_{1-5} alkoxy, a C_{1-5} alkylthio, a C_{1-5} alkylsulfonyl, a cyano, a halogen or a di C_{1-5} alkylamino, respectively, except a non-substituted 2-pyridyl;

R_2 represents a hydrogen, a mono or di C_{1-5} alkylcarbamoyl, an optionally substituted C_{1-5} alkyl, an optionally substituted C_{2-5} alkenyl, an optionally substituted C_{2-5} alkynyl, an optionally substituted C_{3-6} cycloalkyl, an optionally substituted aryl or $-Y-R_5$;

Y represents O, CO, CO_2 or SO_2;

R_5 represents an optionally substituted C_{1-5} alkyl, or an optionally substituted aryl;

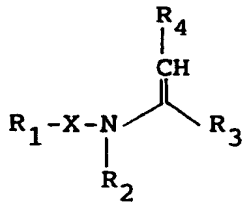
R_3 represents a hydrogen, an optionally substituted C_{1-5} alkyl or an optionally substituted C_{3-6} cycloalkyl;

Z represents N;

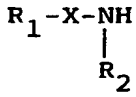
3. An insecticidal composition comprising a compound according to claim 1 as an active ingredient.

4. An insecticidal composition comprising a compound according to claim 2 as an active ingredient.

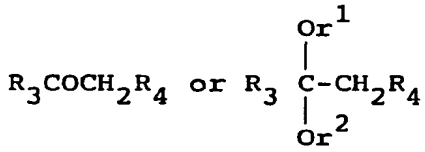
5. A process for the preparation of a compound having the formula



which comprises reacting a compound having the formula

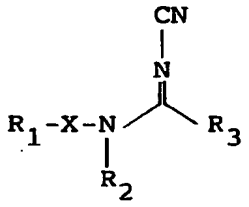


with a compound having the formula

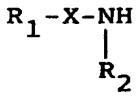


wherein r^1 and r^2 are a C_{1-5} alkyl, respectively; and R_1, R_2, R_3, R_4 and X are as defined above.

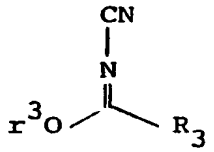
6. A process for the preparation of a compound having the formula



which comprises reacting a compound having the formula

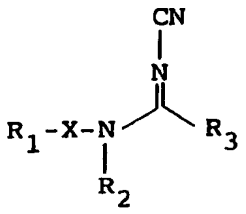


with a compound having the formula

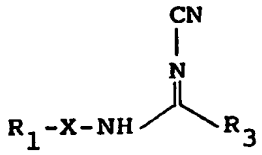


wherein r^3 represents a C_{1-5} alkyl; and R_1, R_2, R_3 and X are as defined above.

7. A process for the preparation of a compound having the formula



which comprises reacting a compound having the formula

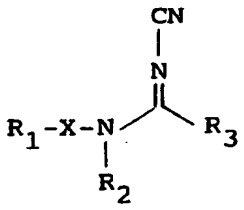


with a compound having the formula

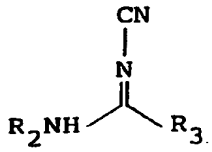
R_2-Hal

wherein Hal represents a halogen atom; and R_1, R_2, R_3 and X are as defined above.

8. A process for the preparation of a compound having the formula



which comprises reacting a compound having the formula

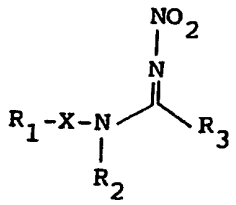


with a compound having the formula

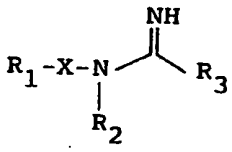
R_1-X-Hal

wherein R_1, R_2, R_3, X and Hal are as defind above.

9. A process for the preparation of a compound having the formula



which comprises reacting a compound having the formula



with nitration reagent,

wherein R_1, R_2, R_3 and X are as defined above.

INTERNATIONAL SEARCH REPORT

International Application No PCT/JP 90/01282

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC5: C 07 D 213/36, 213/40, 213/60, 417/12, 239/26, 237/08
241/12, 231/10, 277/08, A 01 N 43/40, 43/36, 43/48, 43/78

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
IPC5	C 07 D; A 01 N

Documentation Searched other than Minimum Documentation to the Extent that such Documents are included in Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category *	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
A	EP, A2, 0302389 (TAKEDA CHEMICAL INDUSTRIES, LTD.) 8 February 1989, see the whole document	1-9
A	EP, A2, 0302833 (CIBA-GEIGY AG) 8 February 1989, see the whole document	1-9
A	EP, A1, 0306696 (CIBA-GEIGY AG) 15 March 1989, see the whole document	1-9
A	EP, A2, 0303570 (CIBA-GEIGY AG) 15 February 1989, see the whole document	1-9

* Special categories of cited documents:[10]

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
12th December 1990	15. 01. 91
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	miss T. MORTENSEN

Form PCT/ISA/210 (second sheet) (January 1985)

III. DOCUMENTS CONSIDERED T BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	Chemical Abstracts, volume 88, no. 1, 2 January 1978, (Columbus, Ohio, US), Kreutzberger, Alfred: "Antimycotics. VI. Dehydro-N-Mannich bases from cyclic and mixed aliphatic-aromatic amines. ", see page 580, abstract 6816j, & Chem.-Ztg. 1977, 101(9), 400- 401 --	1-9
A	Chemical Abstracts, volume 94, no. 13, 30 March 1981, (Columbus, Ohio, US), see page 691, abstract 102861q, & JP, A, 80130950 (B-Alkoxyacrylonitriles, 3-aminoacrylonitriles, and 2-cyanovinyl esters.) 29 March 1979 --	1-9

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. PCT/JP 90/01282

SA 40597

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 01/11/90
The European Patent office is in no way liable for theseparticulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A2- 0302389	08/02/89	JP-A-	2000171	05/01/90
EP-A2- 0302833	08/02/89	AU-D-	2051088	09/03/89
		JP-A-	1070468	15/03/89
		US-A-	4918086	17/04/90
EP-A1- 0306696	15/03/89	JP-A-	1070467	15/03/89
		US-A-	4948798	14/08/90
EP-A2- 0303570	15/02/89	JP-A-	1070469	15/03/89